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Silica capping for $Al_{0.3}Ga_{0.7}As/GaAs$ and $In_{0.2}Ga_{0.8}As/GaAs$ quantum well intermixing

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Spin-on silica capping has been demonstrated to be an effective dielectric encapsulant layer for quantum well (QW) intermixing at temperatures significantly lower than for conventionally deposited silica. A blueshift of up to 125 meV was observed in the photoluminescence (PL) peak energy of both GaAs and InGaAs QWs after annealing for less than 60 s at 850 °C, without noticeable degradation in the PL emission intensity. A threshold temperature was identified below which no significant QW disordering took place. The activation energy for Al diffusion in $Al_{0.3}Ga_{0.7}As/GaAs$ QWs was about 2.55 eV. Broadly similar effects were seen for $In_{0.2}Ga_{0.8}As/GaAs$ QWs but, in addition, strain effects appear to enhance disordering during the early stages of the anneal. © *1998 American Institute of Physics.* [S0003-6951(98)00649-4]

For monolithic integration of active and passive optoelectronic components, straightforward realization requires postgrowth conversion of a semiconductor heterostructure into a pattern of transparent and absorbing regions. The absorbing sections become light sources and detectors, while the transparent sections could be used for low-loss waveguides, phase modulators, or distributed Bragg reflectors. Postgrowth control of quantum well (QW) profiles is, therefore, of prime importance for the development of photonic integrated circuits.

A number of approaches have been investigated to achieve this goal, such as, selective area epitaxy to produce QWs with different compositions and thickness on a single substrate,[1,2] and post-tuning of the QW band gap by impurity-induced intermixing or by impurity-free vacancy-enhanced intermixing.[3] Compared with impurity-induced intermixing, vacancy-enhanced intermixing is more promising because it can retain high crystal quality, maintain low optical propagation losses, and does not introduce significant changes in free-carrier concentrations. Vacancy-enhanced QW intermixing relies on generation followed by redistribution of Ga vacancies in a structure using a dielectric capping layer such as SiO_2, which acts as a Ga sink at elevated temperatures.[4–6]

Spin-on silica is often used as a dielectric material in device processing as a thin layer can be uniformly spun on a wafer. Using commercial silica products and well-developed spin-coating facilities in a clean-room environment, the properties of hardened spin-on silica capping layers can be controlled reproducibly. A potential application of silica capping for monolithically fabricating optical devices was recently demonstrated.[7] Here, we report details of $Al_{0.3}Ga_{0.7}As/GaAs$ and $In_{0.2}Ga_{0.8}As/GaAs$ QW intermixing using a spin-on silica capping layer together with rapid thermal annealing.

$Al_{0.3}Ga_{0.7}As/GaAs$ and $In_{0.2}Ga_{0.8}As/GaAs$ QW structures were grown by metal organic vapor phase epitaxy. For the $Al_{0.3}Ga_{0.7}As/GaAs$ structure, 300 nm of GaAs were grown on a GaAs substrate, followed by a 100 nm thick $Al_{0.3}Ga_{0.7}As$ barrier layer. A 36.8 Å GaAs QW was then grown, followed by a 50 nm thick $Al_{0.3}Ga_{0.7}As$ upper barrier and a 100 nm thick GaAs cap. For the $In_{0.2}Ga_{0.8}As/GaAs$ structure, a 65 Å thick $In_{0.2}Ga_{0.8}As$ well was grown on a 300 nm thick GaAs buffer layer and capped by 250 nm of GaAs. All the epitaxial layers were undoped. A thin silica layer was formed by spinning commercial liquid silica on the surface at a rotation speed of 3000 rpm for 30 s. The spin-coating process was repeated after an interval of 10 s, which resulted in a silica capping layer with a total thickness of 2000 ± 60 Å. The coated wafers were then baked at 300 °C for 2 h in air. The refractive index of the spin-on silica capping layers was 1.44, comparable to that of conventionally deposited SiO_2 (1.46). The samples were then annealed in a forming gas atmosphere in a rapid annealing furnace. The temperature was controlled by an *in situ* monitoring pyrometer. During annealing, samples were placed face down on an epiready GaAs substrate to minimize desorption of As and possible contamination. Photoluminescence (PL) measurements were performed at 8 K. The excitation source was an Ar^+ laser tuned to a wavelength of 488 nm.

The PL spectra of $In_{0.2}Ga_{0.8}As$ and $Al_{0.3}Ga_{0.7}As$ QWs before and after annealing for 30 s at 750 and 850 °C are illustrated in Fig. 1. As can be seen, a blueshift in the PL peak energy is evident for both QW structures even at an annealing temperature as low as 750 °C, when using a spin-on silica capping layer. At 850 °C, a more significant

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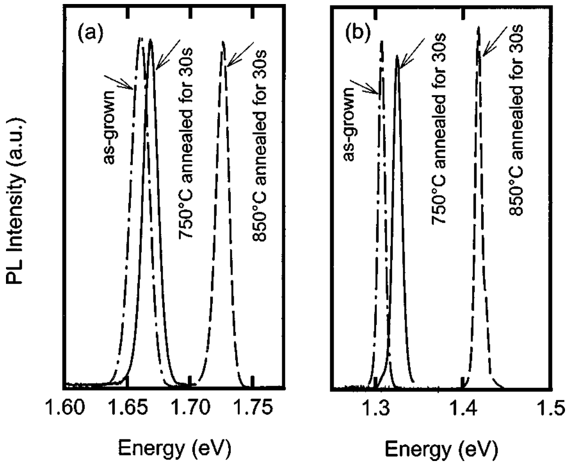

FIG. 1. Low-temperature (8 K) photoluminescence spectra of $In_{0.2}Ga_{0.8}As/GaAs$ and $Al_{0.3}Ga_{0.7}As/GaAs$ quantum wells before and after annealing for 30 s at 750 and 850 °C. (a) $Al_{0.3}Ga_{0.7}As/GaAs$ QW; (b) $In_{0.2}Ga_{0.8}As/GaAs$ QW.

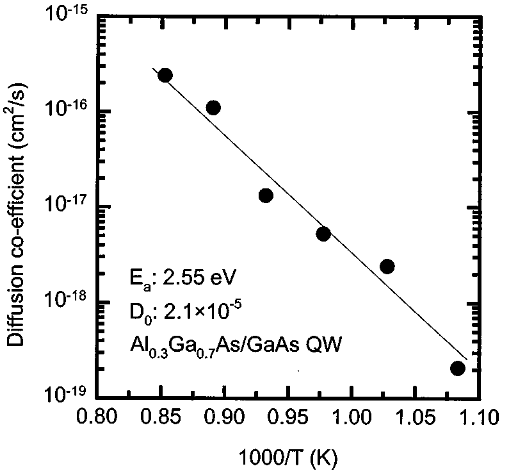

FIG. 3. Diffusion coefficient of Al across an $Al_{0.3}Ga_{0.7}As/GaAs$ heterojunction in an $Al_{0.3}Ga_{0.7}As/GaAs$ QW as a function of reciprocal annealing temperature.

blueshift was obtained. For the same annealing process, a larger blueshift occurs for $In_{0.2}Ga_{0.8}As/GaAs$ than for $Al_{0.3}Ga_{0.7}As/GaAs$ QWs. No noticeable change in the PL peak width and intensity could be seen, even after annealing for up to 60 s at temperatures up to 925 °C. This confirms that QW intermixing using a spin-on silica layer does not significantly degrade the optical properties of QWs. Five samples cleaved from one wafer were subjected separately to the process described above. The PL peak shifts of all annealed samples were almost identical, indicating good reproducibility of the silica coating as well as of the QW intermixing. Samples without a spin-on silica layer were also subjected to the same annealing cycle. No significant QW intermixing induced PL peak shift was observed even at the higher temperatures.

The annealing temperature was increased from 600 to 950 °C for a fixed annealing time of 30 s. The results, presented in Fig. 2, clearly show the existence of a threshold temperature. Below the threshold temperature, the PL peak energy only increases slightly with annealing temperature, but above the threshold temperature the blueshift increases substantially. It can be seen in Fig. 2 that the threshold temperature for both types of QW is about 750 °C. For comparison, SiO_2 deposited using plasma-enhanced chemical vapor deposition was also used as the dielectric layer, and a $In_{0.2}Ga_{0.8}As/GaAs$ QW was subjected to the same annealing process. We found that the threshold temperature in this case was about 840 °C. Hence, the use of spin-on silica as a dielectric layer for QW intermixing reduces the threshold temperature at which significant QW intermixing takes place by about 90 °C.

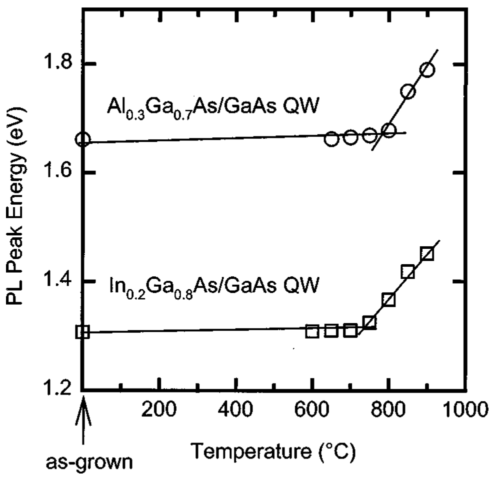

FIG. 2. Low-temperature (8 K) photoluminescence peak energy of $In_{0.2}Ga_{0.8}As/GaAs$ and $Al_{0.3}Ga_{0.7}As/GaAs$ quantum wells as a function of annealing temperature. Annealing time was 30 s. Solid lines are to guide the eye.

For AlGaAs/GaAs and InGaAs/GaAs structures, QW intermixing is a result of interdiffusion of group III atoms on substitutional lattice sites across heterojunctions. The amount of QW intermixing depends on the concentration of group III vacancies.[8,9] The blueshift in the PL peak energy observed at annealing temperatures below the threshold temperature most likely arises from QW intermixing caused by redistribution of intrinsic defects.[10] The concentration of intrinsic defects is actually quite small, so little QW intermixing takes place. Only at a high enough temperature, can chemical reactions take place at the silica–GaAs interface to produce a large number of Ga vacancies in the GaAs adjacent to the interface. Driven by a concentration gradient, the flux of injected nonthermal equilibrium Ga vacancies results in substantially enhanced interdiffusion of group III atoms across heterojunctions. So, the threshold temperature, as observed in Fig. 2, represents the minimum temperature required for effective chemical reactions at the silica–GaAs interface. The diffusion coefficient of Al in $Al_{0.3}Ga_{0.7}As/GaAs$ was calculated theoretically using the results presented in Fig. 2. Data are fitted well by an Arrhenius function of the form $D=D_0\exp(-E_a/kT)$ over the entire annealing temperature region (see Fig. 3). The activation energy (E_a) was 2.55 eV and the prefactor (D_0) was 2.1×10^{-5} cm^2/s. This activation energy is actually lower than previous reports obtained using conventionally deposited SiO_2 as the dielectric layer.[11] These results clearly show that spin-on silica reduces the activation energy for impurity-free vacancy-enhanced disordering in GaAs and InGaAs QWs. Possible reasons for this include effects related either to the film density or to the surface bonding with GaAs.

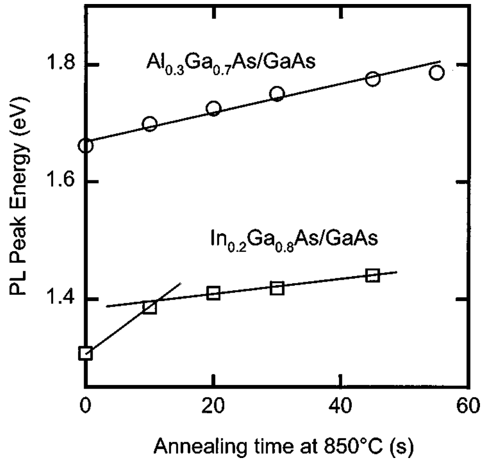

FIG. 4. Low-temperature (8 K) photoluminescence peak energy of $In_{0.2}Ga_{0.8}As/GaAs$ and $Al_{0.3}Ga_{0.7}As/GaAs$ QWs as a function of annealing time. Annealing temperature was 850 °C. Solid lines are to guide the eye.

Figure 4 shows the effect of prolonged annealing at 850 °C. The blueshift of the $Al_{0.3}Ga_{0.7}As/GaAs$ QW increases almost linearly with increasing annealing time, suggesting that saturation of Ga atoms in the silica has not yet occurred under these conditions. By contrast, for the $In_{0.2}Ga_{0.8}As/GaAs$ QW, a large initial blueshift is evident after an annealing time of just 15 s at 850 °C, followed by a much slower but linear increase of the PL peak energy with increasing annealing time. It has been reported that the strain in $In_{0.2}Ga_{0.8}As/GaAs$ QWs influences the intrinsic defect concentration and, therefore, the diffusivity of group-III atoms.[12] We also believe that at 850 °C, the QW intermixing is promoted by the strain. After a certain amount of QW intermixing, the reduced lattice mismatch dilutes the strain effect. As for the $Al_{0.3}Ga_{0.8}As/GaAs$ QW, further intermixing of the $In_{0.2}Ga_{0.8}As/GaAs$ QW has a linear dependence on annealing time (see Fig. 4).

In conclusion, spin-on silica capping can be used as an effective dielectric encapsulant for QW intermixing. The threshold temperature for Ga vacancy-enhanced QW intermixing is about 750 °C. A low activation energy (2.55 eV) for Al diffusion in $Al_{0.3}Ga_{0.7}As/GaAs$ QW using a silica capping layer makes it possible to conduct QW intermixing at relatively low annealing temperatures. At 850 °C, a blueshift of up to 125 meV in the PL peak energy has been demonstrated after less than 60 s annealing time. A linear increase of the PL peak energy with increasing annealing time was observed for $Al_{0.3}Ga_{0.7}As/GaAs$ QWs. Strain-enhanced intermixing appears to play a role in $In_{0.2}Ga_{0.8}As/GaAs$ QWs, which leads to a rapid blueshift of the PL peak energy during an initial QW intermixing stage.

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